Investigating and Quantifying CO_2-Fluid-Shale Interactions

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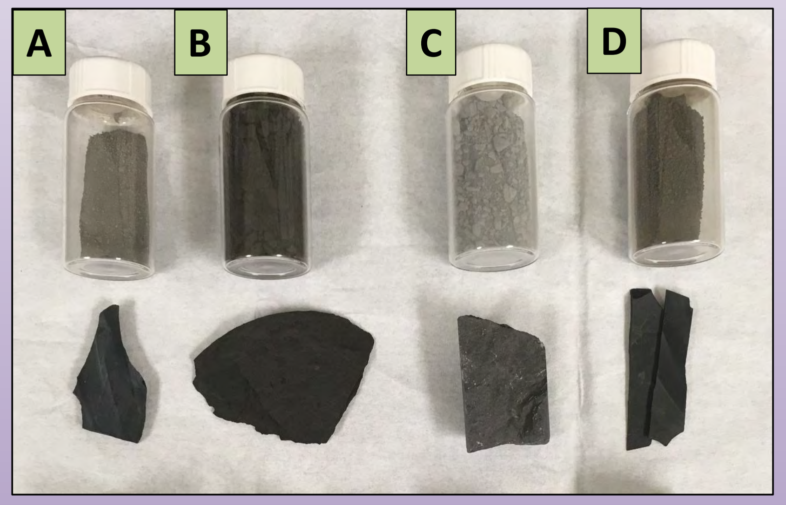
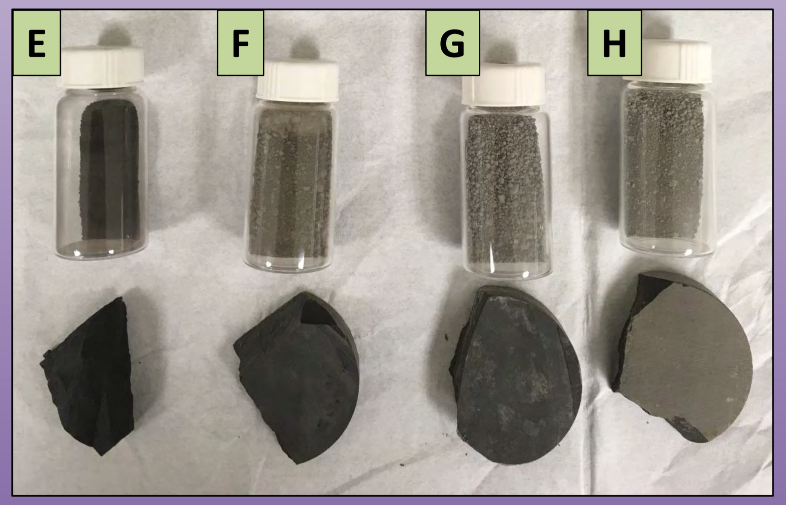
Abstract

Investigating and quantifying the interactions that occur between CO_2, fluids, and shale is becoming increasingly important. These interactions will play a large role when (1) storing CO_2 in hydraulically fractured shale formations, (2) utilizing CO_2 as a hydraulic fracturing fluid, and (3) determining if CO_2 can be an effective agent for enhanced hydrocarbon recovery. Regardless of the reason, as CO_2 is injected into a shale formation, it will interact with shale components (i.e. organic matter, minerals, cations/anions) driving various reactions that will alter the rock properties. The alteration of these properties, such as porosity or permeability, will impact the permeance of CO_2 storage and the effectiveness of CO_2 to work as a fracturing or hydrocarbon extraction agent. To examine these alterations, Marcellus and Utica shale samples were analyzed in the presence of CO_2 and fluid (water). Techniques used include feature relocation scanning electron microscopy (SEM), surface area and pore size analysis using volumetric gas sorption and density functional theory (DFT) methods, and in-situ Fourier Transform Infrared (FTIR) spectroscopy. Feature relocation SEM showed little alteration before and after dry and wet CO_2 exposure in the silicate rich Marcellus Shale (MS-1) sample. However, the carbonate rich Marcellus Shale (MS-4) and Utica Shale (US-1) samples experienced minor etching with dry CO_2 and significant carbonate dissolution and precipitation with wet CO_2. After exposure to CO_2 and water, the Brunauer-Emmett-Teller (BET) surface area of the silicate rich Marcellus Shale increased while the carbonate rich Marcellus Shale decreased. FT-IR spectroscopy indicates formation and dissolution of carbonate species in hydrated carbonate rich shales which buffer as a function of pH with exposure to CO_2 and pressure. Current in-situ FT-IR results are limited to fully saturated samples or completely dry samples. A new system set up, designed to control relative humidity and allow examination of partially hydrated samples, is presented.

Samples





A: US-1
Utica Shale (outcrop)

B: US-PZ
Utica Shale (Prod. Zone)

C: US-AD
Utica Shale (At Depth)

D: MS-1
Marcellus Shale

E: MS-4
Marcellus Shale

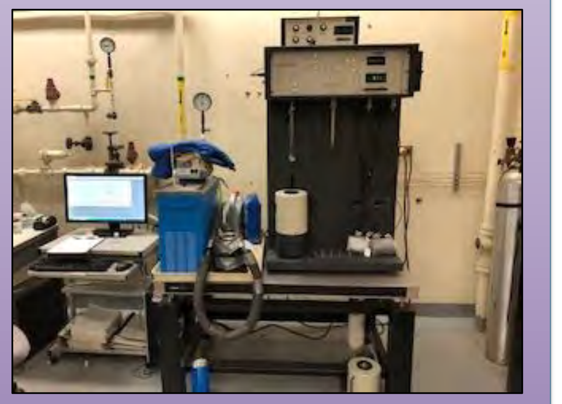
F: EFS-1
Eagleford Shale

G: MAN-1
Mancos Shale

H: BS-1
Barnett Shale

Instruments

Scanning Electron Microscope used for feature relocation before and after dry/wet CO_2 exposure.



Quantachrome Autosorb 1-C used to analyze surface area and pore size for shale samples.

Hiden microbalance (IGA) used for gravimetric gas adsorption isotherm analysis.

IR Relative Humidity System

A: Gas inlet from cylinders

B: Micro metering valve for dry gasses

C: Micro metering valve for wet gasses

D: Fluid drip tube

E: Pressure transducer

F: Pressure reader

G: Relative humidity probe

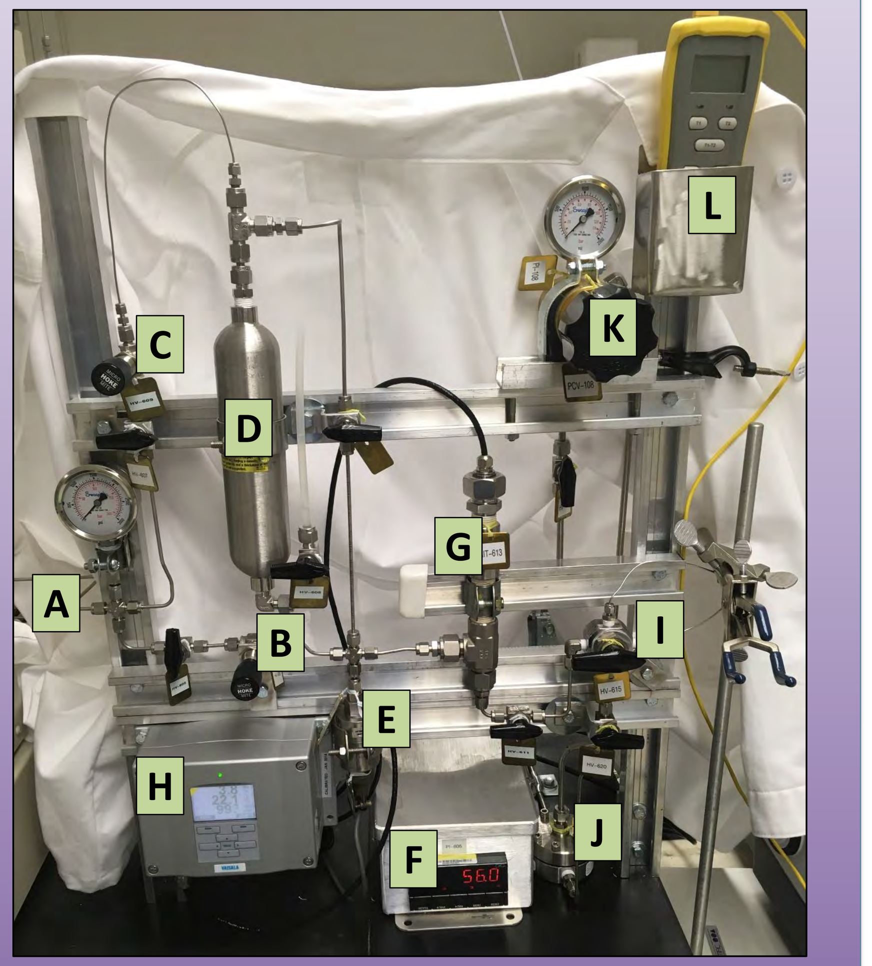
H: Relative humidity reader

I: Gas outlet to sample cell

J: Back pressure diaphragm

K: Back pressure regulator

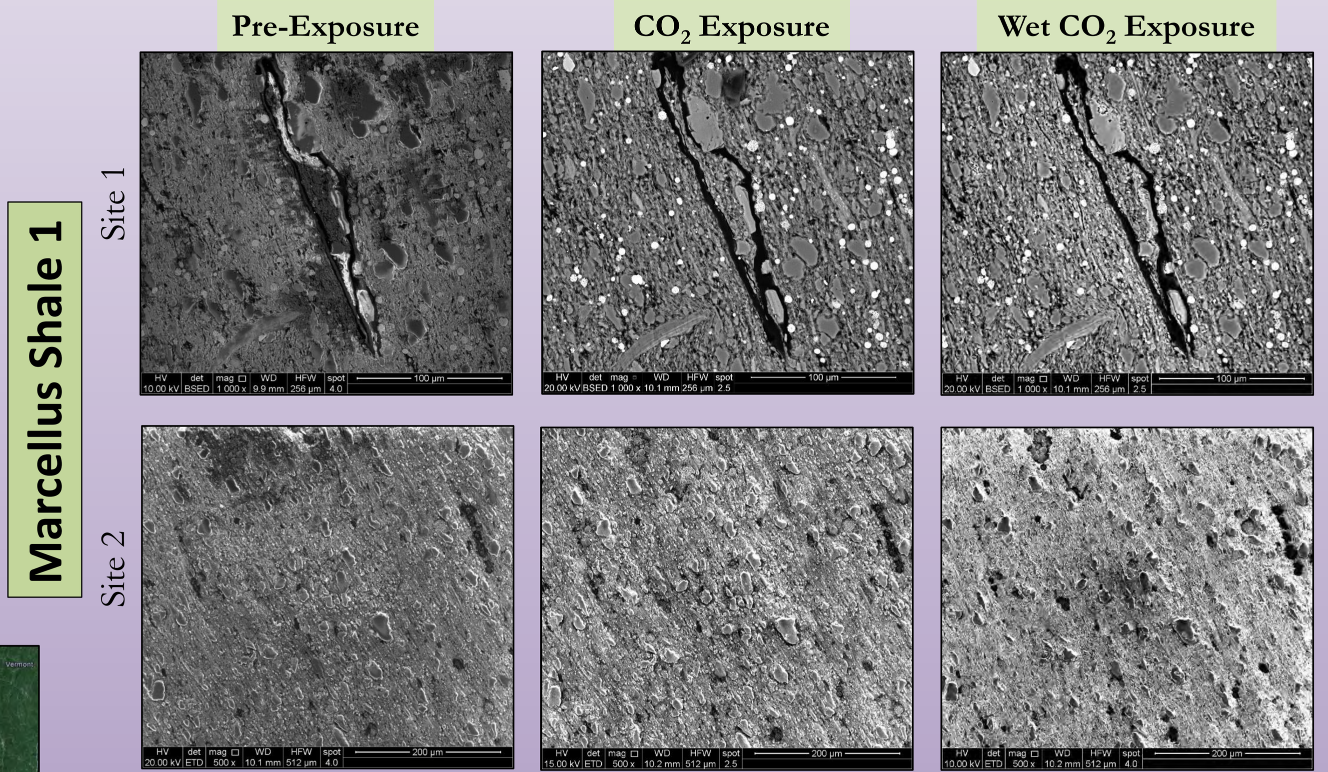
L: Temperature reader

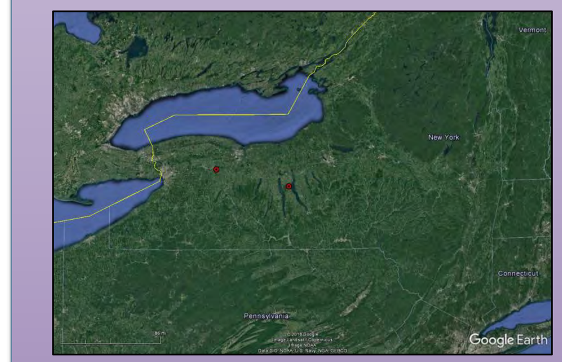


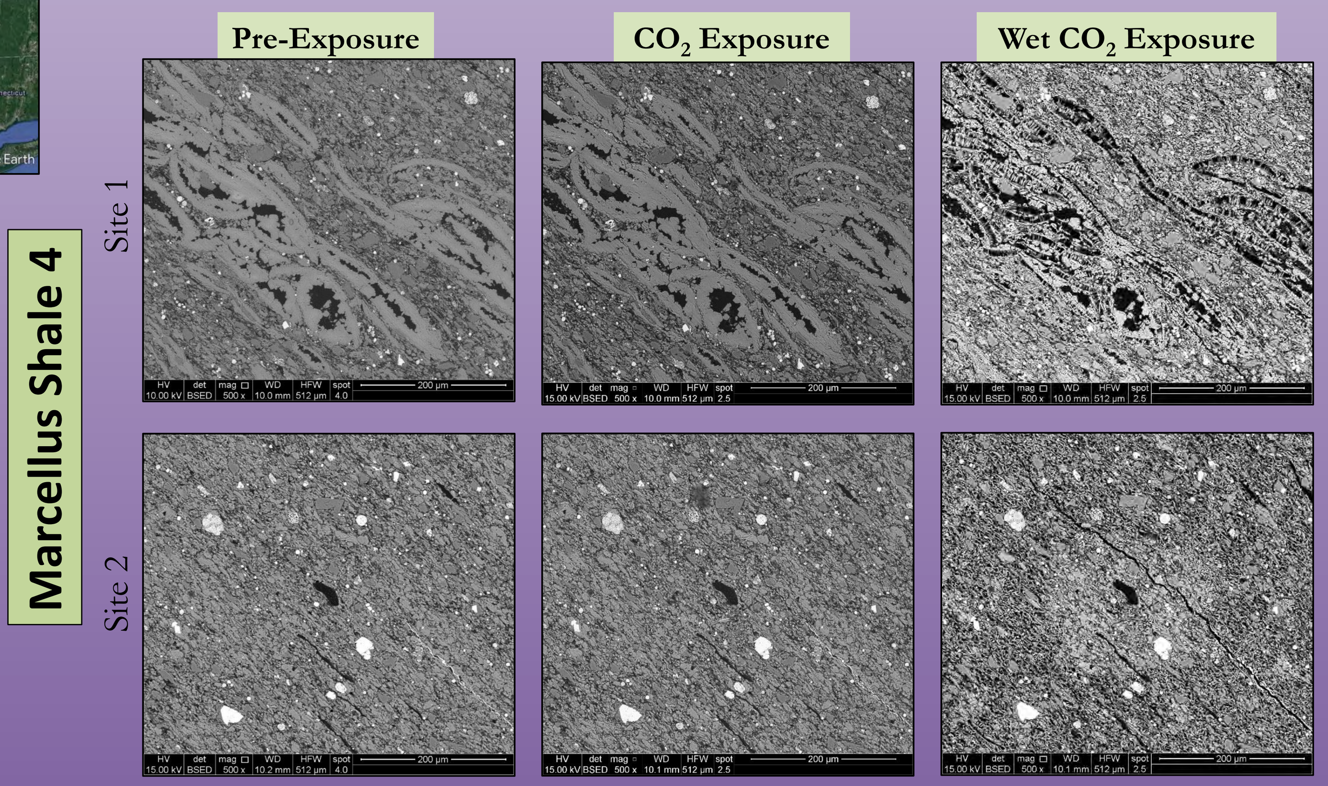
Relative humidity set up for infrared spectroscopy.

Scanning Electron Microscopy: Results

SEM-BSE-ETD (Scanning Electron Microscopy Backscattered Electron – site 1 and Everhart Thornley Detector – site 2) images of Marcellus shale sample MS-1 before exposure, exposed to dry $scCO_2$ and exposed to wet $scCO_2$. Minor changes were observed after dry $scCO_2$ exposure primarily in the form of mineral phase dissolution. Significant alterations were observed after exposure to wet $scCO_2$ appearing to increase pore space from carbonate dissolution.







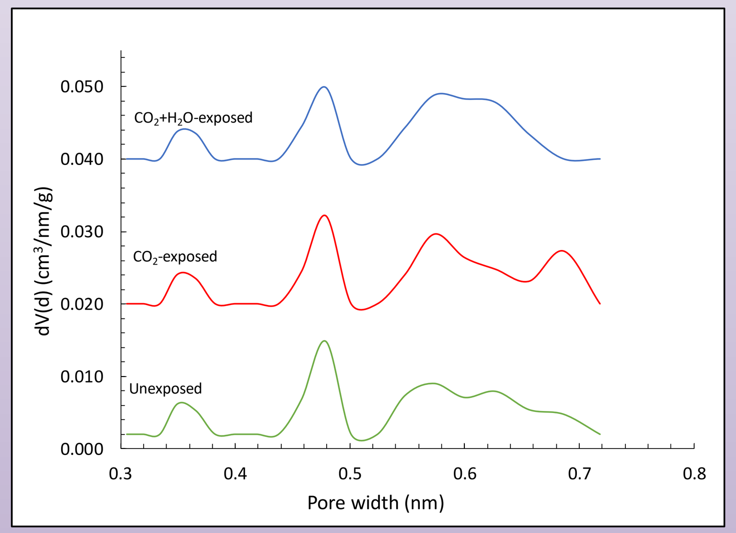
SEM-BSE (Scanning Electron Microscopy Backscattered Electron) images of Marcellus shale sample MS-4 before exposure, exposed to dry $scCO_2$ and exposed to wet $scCO_2$. There is no observable difference between the pre-exposed and dry scCO2 exposed sample. There was considerable alteration observed once the sample was expose to wet $scCO_2$. Alterations included: dissolution of carbonate and fracture propagation.

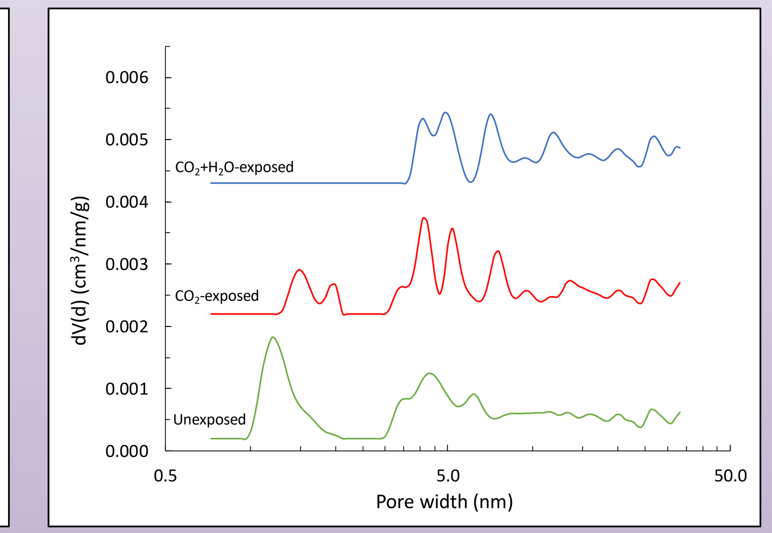
Surface Area and Pore Size Analysis: Results

US-1

Pore size distribution of US-1 based on CO_2 (left) and N_2 (right) isotherm characterization.

BET surface area = 5.8-6.8 (m^2/g).

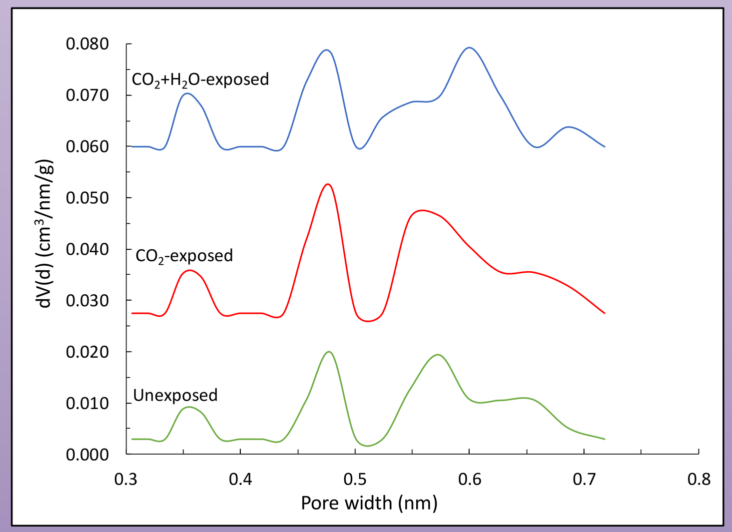


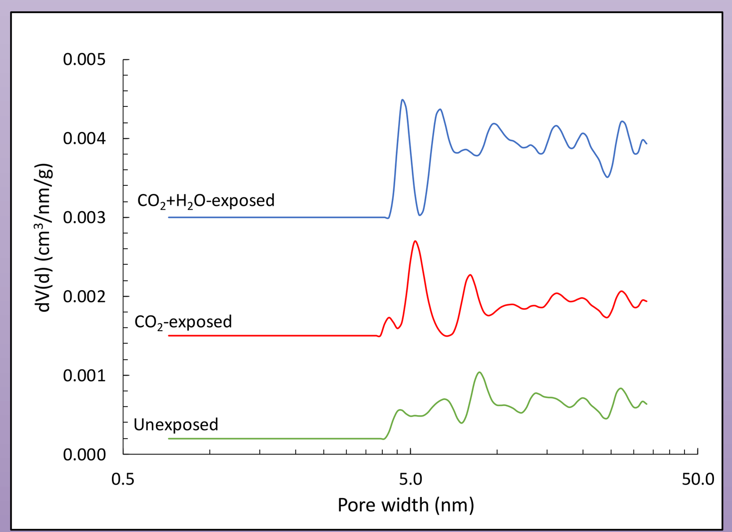


MS-1

Pore size distribution of MS-1 based on CO_2 (left) and N_2 (right) isotherm characterization.

BET surface area = 3.7-8.3 (m^2/g).

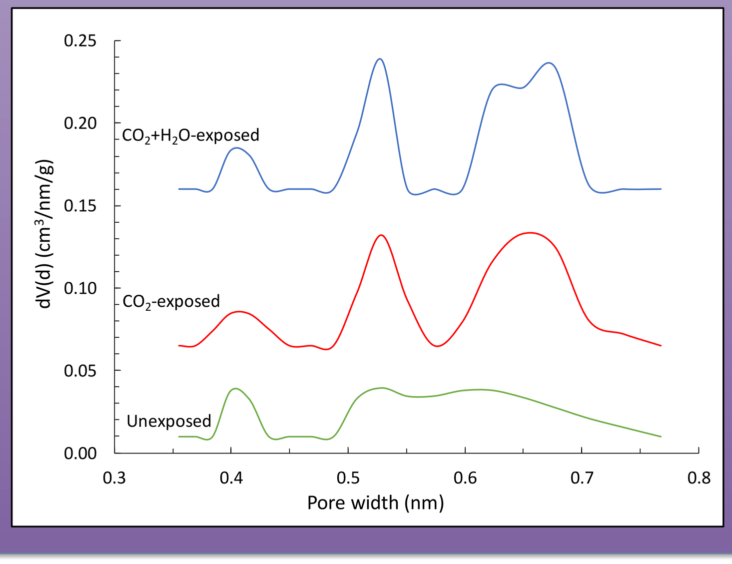


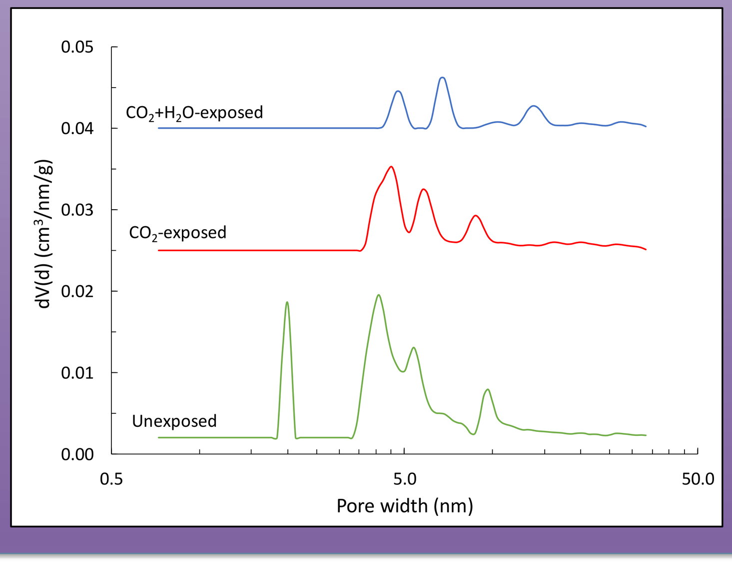


MS-4

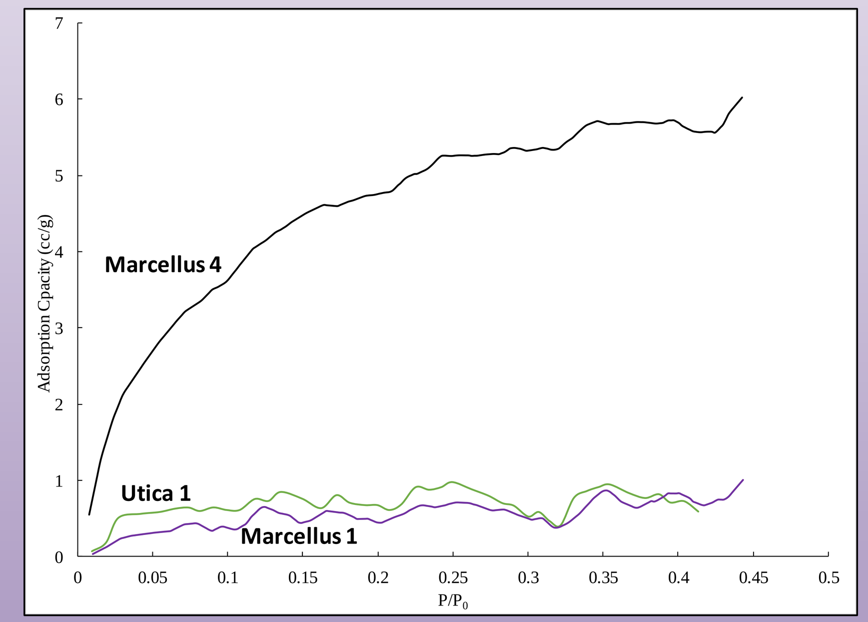
Pore size distribution of MS-4 based on CO_2 (left) and N_2 (right) isotherm characterization.

BET surface area = 12.1-49.5 (m^2/g).





Adsorption Isotherms



Top: CO_2 adsorption isotherms for US-1, MS-1, and MS-4.

Bottom: Table of carbon content - organic and inorganic. Note the effect carbon content has on CO_2 adsorption.

Sample ID	Total Carbon		Total Inorganic Carbon		Total Organic Carbon	
	Carbon (%)	Std. Dev.	Carbon (%)	Std. Dev.	Carbon (%)	Std. Dev.
MS-1	6.64	0.21	0.13	0.06	6.51	0.22
MS-4	14.7	0.2	5.5	0.06	9.2	0.6
US-1	9.86	0.08	9.41	0.14	0.45	0.17

References

- Dieterich, M., Kutchko, B., Goodman, A., 2016. Characterization of Marcellus Shale and Huntersville Chert before and after exposure to hydraulic fracturing fluid via feature relocation using field-emission scanning electron microscopy. Fuel, p. 227-235.
- Goodman, A. L., Campus, L. M., Schroeder, K. T., 2005. Direct Evidence of Carbon Dioxide Sorption on Argonne Premium Coals Using ATR-FTIR Spectroscopy. Energy & Fuels, v. 19, p. 471-476.
- Kutchko, B.G., Goodman, A.L., Rosenbaum, E., Natesakhawat, S., Wagner, K., 2013. Characterization of coal before and after supercritical CO2 exposure via feature relocation using field-emission scanning electron microscopy. Fuel, v. 107, p. 777-786.
- Levine, J.S., Fukai, I. Soeder, D.J., Bromhal, G., Dilmore, R.M., Guthrie, G.D., Rodosta, T., Sanguinito, S., Frailey, S., Gorecki, D., Peck, W., Goodman, A.L., 2016. U.S. DOE NETL Methodology for Estimating the Prospective CO2 Storage Resource of Shales at the National and Regional Scale. International Journal of Greenhouse Gas Control, v. 51, p. 81-94.
- Sanguinito, S., Goodman, A., Tkach, M., Barbara, K., Culp, J., Natesakhawat, S., Fazio, J., Fukai, I., Crandall, D., 2018, Quantifying dry supercritical CO2-induced changes of the Utica Shale: Fuel, v. 226, p. 54-64.
- Steefel, C.I., Molins, S., Trebotich, D., 2013. Pore scale processes associated with subsurface CO_2 injection and sequestration. Reviews in Mineralogy and Geochemistry. v. 77. p. 259-303.
- US-DOE-NETL, 2015. Carbon Storage Atlas, fifth edition. U.S. Department of Energy—National Energy Technology Laboratory—Office of Fossil Energy.

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